



Mineral materials as feasible amendments to stabilize heavy metals in polluted urban soils

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Abstract

Four minerals, agricultural limestone (AL), rock phosphate (RP), palygorskite (PG), and calcium magnesium phosphate (CMP), were evaluated by means of chemical fractions of heavy metals in soils and concentrations of heavy metals in leachates from columns to determine their ability to stabilize heavy metals in polluted urban soils. Two urban soils (calcareous soil and acidic soil) polluted with cadmium, copper, zinc and lead were selected and amended in the laboratory with the mineral materials for 12 months. Results indicated that application of the mineral materials reduced exchangeable metals in the sequence of Pb, Cd > Cu > Zn. The reduction of exchangeable fraction of heavy metals in the soils amended with different mineral materials followed the sequence of CMP, PG > AL > RP. Reductions of heavy metals leached were based on comparison with cumulative totals of heavy metals eluted through 12 pore volumes from an untreated soil. The reductions of the metals eluted from the calcareous soil amended with the RP, AL, PG and CMP were 1.98%, 38.89%, 64.81% and 75.93% for Cd, 8.51%, 40.42%, 60.64% and 55.32% for Cu, 1.76%, 52.94%, 70.00% and 74.12% for Pb, and 28.42%, 52.74%, 64.38% and 49.66% for Zn. Those from the acidic soil amended with the CMP, PG, AL, and RP were 25.65%, 68.06%, 78.01% and 79.06% for Cd, 26.56%, 49.64%, 43.40% and 34.68% for Cu, 44.44%, 33.32%, 61.11% and 69.44% for Pb, and 18.46%, 43.77%, 41.98% and 40.68% for Zn. The CMP and PG treatments were superior to the AL and RP for stabilizing heavy metals in the polluted urban soils.

Key words: heavy metals; polluted soil; chemical fraction; chemical immobilization; mineral materials

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Introduction

Heavy metal pollution of soil is an increasingly urgent problem all over the industrialized world. Heavy metals, unlike organic contaminants, are generally immutable, not degradable and persistent in soil. High concentrations of heavy metals in soils may cause long-term risks to ecosystems and humans (Alloway, 1995). It is well known that urban soils receive significant amounts of heavy metals such as Cd, Cu, Pb, and Zn from traffic, smelting activities, dust deposition from fossil fuel combustion, industrial activities and waste disposal. Heavy metals can also be accumulated in the topsoil from atmospheric deposition (Pandey and Pandey, 2009). This is certainly an important issue, considering that relatively high metal contents are often found in soil of urban areas. Unlike soils in rural areas, urban soils are seldom related with mass food production. However, they still can have a direct influence on human health, as they can be transferred into the human body by inhalation of contaminated suspended

particles, soil ingestion, with special attention for children in playground areas via hand-to-mouth, dermal absorption by direct contact, or contamination of groundwater (Pruvot et al., 2006). Therefore, the target for remediation of heavy metal contaminated urban soils should be to reduce the solubility and mobility of heavy metals in the soils. *In situ* stabilization of heavy metals in the urban soils can be considered a promising alternative remediation path used to reduce mobility of the heavy metals in the soils by adding immobilizing agents.

A wide array of techniques have been proposed to remediate heavy metal-contaminated soils (van Herwijnen et al., 2007; Farrell et al., 2010). The remediation techniques of heavy metals in soils include physical remediation, chemical remediation, phytoremediation, and agro-ecological engineering techniques (Jadia and Fulekar, 2009; Tandy et al., 2009). Physical remediation technologies based on the excavation, removal, washing, and landfilling of metal contaminated soils are highly effective at lowering risk. However, they are expensive to implement. Although phytoremediation, i.e., use of plants for ameliorating metal-contaminated sites, has received

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considerable attention in recent years (McGrath et al., 2002), one of the major problems associated with this approach is low metal removal rates (Pierzynski et al., 2000; McGrath et al., 2002). In addition, phytoremediation is of limited applicability in urban soils. In order to obtain low-cost remediation methods and *in situ* inactivation techniques, soil chemical amendments have been recently investigated, appearing as potential valuable alternative techniques for a wide range of polluted sites (Fayiga and Ma, 2006). *In situ* chemical remediation stabilized heavy metals by adding some nontoxic materials into soils. It is a remediation technique that decreases the concentration of dissolved contaminants by sorption or precipitation, and limits the transport of pollutants into deeper soil layers, eventually into groundwater (Perez-de-Mora et al., 2007). Compared with other remediation techniques, *in situ* chemical immobilization is less expensive and may provide a long-term remediation solution through the formation of low solubility minerals and/or precipitates.

Many natural or synthetic materials have been tested, mainly in the last decades, to evaluate their ability to immobilize toxic heavy metals (Khan and Jones, 2009; Lin and Zhou, 2009; Uchimiya et al., 2010). Research on chemical immobilization of heavy metals includes alkaline- and phosphate-based materials that adsorb, chelate, or complex heavy metals in soils. Alkaline materials used as chemical immobilization treatments include calcium oxides, fly ash, and calcium and magnesium carbonates (Filius et al., 1998; Derome, 2000). They can reduce heavy metal solubility in soil by increasing soil pH and concomitantly increasing metal sorption to soil particles (Vangronsveld et al., 1995; Filius et al., 1998; Boisson et al., 1999). Phosphate materials, independently of the sources, lessen dramatically lead solubility by its precipitation as pyromorphite-like minerals, and have a great potential to cost-effectively treat Pb-polluted soils. Phosphate rocks have been also tested to remediate soils polluted with zinc, cadmium or copper (Boisson et al., 1999). Other materials evaluated as soil amendments to stabilize Zn, Cd, Cu or Pb-polluted soils include zeolites (Chlopecka and Adriano, 1997), iron, manganese and aluminium oxides and oxyhydroxides and waste byproducts rich in these oxides (Boisson et al., 1999; Singh and Agrawal, 2010), clay minerals (Badora et al., 1998) and organic materials (compost, peat, manure, etc.) (Shuman et al., 2002). In general, these treatments lower the risk of polluted soils limiting metal leaching and bioavailability.

In spite of this large amount of work studying the use of different materials as soil amendments, only a very few have been performed with clay minerals such as palygorskite. Most research efforts investigating chemical immobilization treatments have focused on reducing the

bioavailability of metals in agricultural soils. However, it is unclear whether the soil amendments influence transformation and mobility of heavy metals in urban soils. It is necessary to understand the effect of chemical treatments for reducing the mobility and transport of heavy metals in the urban soils. Therefore, the objective of this study was to evaluate the effects of inexpensive, commonly available mineral materials, agricultural limestone, rock phosphate, palygorskite, and calcium magnesium phosphate, on chemical transformation of heavy metals in the contaminated urban soils, and to compare the ability of the amendments to reduce the solubility and transport of heavy metals present in contaminated soils.

1 Materials and methods

1.1 Soils, amendments and incubation experiment

Two urban soils (calcareous soil and acidic soil) with moderate to relatively high cadmium, copper, zinc and lead contents (Table 1), were sampled (0–20 cm) from green areas of Hangzhou, China, located in different zones of the city. Calcareous soil (soil 1) was collected from the commercial area, and acidic soil (soil 2) was collected from a former manufacture area. Soils were dried at room temperature, sieved (2 mm) and amended in the laboratory with four mineral materials: agricultural limestone (AL), rock phosphate (RP), palygorskite (PG), and calcium magnesium phosphate (CMP), at two rates (2%, 5%, W/W). Four mineral materials were purchased from local markets. AL had 98% effective calcium carbonate equivalent as CaCO_3 , and contained 3.12 mg/kg of Cd, 14.3 mg/kg of Cu, 43 mg/kg of Pb, and 73.1 mg/kg of Zn, and its pH value was 13.1. RP contained 12.1% P-carbonated fluorapatite, and 1.34 mg/kg of Cd, 13.8 mg/kg of Cu, 10.53 mg/kg of Pb, and 114.76 mg/kg of Zn. PG is a hydrated magnesium aluminium silicate mineral with a structure consisting of parallel ribbons of 2:1 layers. PG used in the study contained 65% of palygorskite, 6% of sepiolite, 3% of smectite, and 7% of illite. The concentrations of Cd, Cu, Pb, and Zn in the PG were 0.34, 25.63, 13.76 and 142.12 mg/kg, respectively. CMP contained 18.6% of MgO, 36.2% of CaO, 40.23% of P_2O_5 , 2.67 mg/kg of Cd, 17.2 mg/kg of Cu, 28.2 mg/kg of Pb, 85.4 mg/kg of Zn, and its pH value was 8.3.

A control treatment (CO) for each soil with no amendment addition was also prepared. The experimental design included nine treatments for each soil (CO, AL1, AL2, RP1, RP2, PG1, PG2, CMP1, CMP2, in which 1 and 2 present 2% and 5% of application rates of amendments, respectively). Each treatment was carried out in triplicates. The mixtures were carefully homogenized. Distilled water

Table 1 Physical and chemical properties and metal contents of urban soils

Soil	pH	Cd (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Organic matter (g/kg)	Clay (g/kg)
Calcareous soil	8.22	4.48	143	476	427	32.6	203
Acidic soil	4.63	3.54	524	835	1143	19.8	254

Data are mean of three replicates.

was added up to 75% of their field capacity, and the mixtures were incubated at room temperature ($25 \pm 1^\circ\text{C}$) for 12 months. Moisture was checked monthly by weighing, and water was re-added when necessary. The effects of the amendments on the chemical immobilization of metals in the soils were evaluated by measuring chemical forms of heavy metals and leaching experiment.

1.2 Measurement of soil properties

Soil pH was measured in the supernatant of a 1:2.5 (W/W) soil-water suspensions. Soil samples used for particle-size distribution were pre-treated with H_2O_2 , dispersed overnight in NaOH and then measured by the micropipette method (Miller and Miller, 1987). Soil organic carbon was measured by wet oxidation method. Soil organic matter was determined by the Walkley-Black wet combustion method, and CaCO_3 by a manometric method (Page et al., 1982). Particle size distribution was estimated by the hydrometer method (Gee and Bauder, 1986).

1.3 Fractionation of heavy metals in the incubated soils

A modified procedure of Amacher (1996) was employed to fractionate heavy metals in the incubated soils. This method is based on both solubility of individual solid-phase components and on selectivity and specificity of chemical reagents. The procedure provides a gradient for the physico-chemical association strength between heavy metals and solid components rather than for actual speciation. Therefore, the terms of the fractions are more operationally than chemically defined. Heavy metals in the soil were sequentially fractionated into: (1) exchangeable metals (including water soluble) extracted with 0.1 mol/L $\text{Mg}(\text{NO}_3)_2$ (shaking 2 hr at 80 cycles/min); (2) carbonate associated metals extracted with 1 mol/L sodium acetate at pH 5 (shaking 5 hr at 80 cycles/min); (3) oxide associated metals extracted with 0.2 mol/L ammonium oxalate + 0.2 mol/L oxalic acid + 0.1 mol/L ascorbic acid at pH 3.3 (in a boiling water bath for 30 min); (4) organically-bound associated metals extracted with 30% H_2O_2 at pH 2 (in a boiling water bath for 30 min); and (5) the residual metals extracted by digestion with nitric acid and perchloric acid. After each successive extraction, the supernatant solution was separated by centrifuging at $4500 \times g$ for 30 min and filtered through a quantitative filter paper. The concentrations of Cd and Pb were determinate by a graphite furnace atomic absorption spectrophotometer (GFAAS, Model SIMAA 6000, Perkin-Elmer, USA), and Cu and Zn were determinate by a flame atomic absorption spectrometry (FAAS, Perkin-Elmer, USA). Total Cd, Pb, Cu, and Zn concentrations in the soils were also determined after digestion with nitric acid and perchloric acid.

1.4 Leaching experiment

Chemical immobilization treatments were evaluated using leaching experiments with repacked soil columns. Control soils and soils amended with four mineral materials at application rate of 5% (CO, AL2, RP2, PG2, and CMP2) were used in the leaching experiment. The leaching study was conducted in laboratory using PVC

leaching columns (10 cm i.d., 30 cm length). The bottom of the column was a PVC plate containing several 5-mm-diameter holes. Acidic washed quartz sands was first packed to form a column 5-cm long, and 20-cm incubated soils were next packed in the top of the columns. Soils were packed into columns by consistently tapping the top of the columns while the soils were slowly poured in. The columns were packed with a bulk density of about 1.30 g/cm^3 . Triplicate columns were used for each treatment. Two qualitative filter papers were placed on the top of soil columns to prevent the disturbance by water droplets during leaching. Before leaching, the soils in the columns were adjusted to field capacity moisture content and incubated for 2 days at room temperature. A total of 9.60 L (0.80 L for each of 12 leaching cycles) of deionized water was applied to each soil column at a rate of 10 mL/min. The designed amount of leaching water for each leaching cycle was equivalent to 1 pore volume of soil column (800 mL). Columns were allowed to drain for 46 hr before next leaching water was applied. Preliminary studies showed that a steady state within the column was obtained after 22 hr of pre-equilibration; however, we selected a pre-equilibration period of 46 hr for added insurance of an equilibrated system. Column leachates were collected in 2000-mL beakers below the soil columns, transport into polyethylene bottles for analysis.

Column leachates were filtered through a $0.45 \mu\text{m}$ membrane before analysis. Leachates were then acidified with trace metal grade HNO_3 to pH < 2 (APHA, 1992) prior to metal analysis (Cd, Cu, Pb, and Zn). Soluble metal loads were calculated from metal concentrations and total leachate volumes.

Chemical analyses were performed using calibration curves determined from standards prepared from certified stock solutions. Sample blanks were analyzed to determine and correct for any matrix effects. Heavy metal control standards were used to assess instrument precision and accuracy.

1.5 Data analysis

All statistical analyses were carried out using SAS software, release 6.12. The significant differences in chemical fraction of heavy metals in the soils and concentrations of heavy metals in the leachates from soil columns among different treatments were analyzed statistically by the General Linear Model procedure. Correlation analysis was performed by the Correlation and Mean procedure.

2 Results

2.1 Effect of amendment application on soil pH

Application of amendments had a significant effect on pH value of both studied soils (Table 2). Soil pH value increased with increasing application rates of amendments. When the same rates of amendments were applied, the pH values increased in the sequence of $\text{PG} < \text{RP} < \text{CMP} < \text{AL}$. The differences in increase of pH value may due to the difference of carbonate in the mineral materials.

Table 2 Effect of amendment application on soil pH

Treatment	Rate (g/kg)	Calcareous soil	Acidic soil
CO	0	8.22 ± 0.06 e	4.63 ± 0.04 f
RP1	20	8.37 ± 0.05 d	5.04 ± 0.10 d
RP2	50	8.63 ± 0.07 c	5.26 ± 0.03 c
AL1	20	8.76 ± 0.04 b	5.33 ± 0.04 b
AL2	50	9.02 ± 0.11 a	5.54 ± 0.07 a
PG1	20	8.36 ± 0.08 d	4.87 ± 0.06 e
PG2	50	8.55 ± 0.07 d	5.16 ± 0.08 d
CMP1	20	8.48 ± 0.06 d	5.14 ± 0.07 d
CMP2	50	8.65 ± 0.06 c	5.36 ± 0.05 b

CO: control; RP1 and RP2: application of rock phosphate at 2% and 5%; AL1 and AL2: application of agricultural limestone at 2% and 5%, respectively; PG1 and PG2: application of palygorskite at 2% and 5%; CMP1 and CMP2: application of calcium magnesium phosphate at 2% and 5%.

Mean values followed by the same letter within a column are not different at $p < 0.05$ by Fisher's protected least significant difference.

2.2 Effect of amendment application on chemical forms of heavy metals in the soils

Among the chemical fractions, exchangeable fraction of heavy metals in soils mostly determines the actual environmental risk. Therefore, proportion of exchangeable fraction could be used to evaluate the effect of the amendments on heavy metals immobilization in the urban soils and environmental impact of the metals. Result indicated chemical fractions of Cd, Cu, Pb, and Zn in the soil were affected, in different extent, by application of the mineral materials (Tables 3, 4, 5, and 6), however, the effects varied with soils and heavy metals. RP treatments showed no significant effects on chemical fractions of heavy metals in the calcareous soil. However, it decreased the exchange-

able Cd, Cu, Pb, and Zn in the acidic soil, as compared to CO. AL treatments decreased the exchangeable Cd, Cu, Pb, and Zn in the calcareous soil, and exchangeable Cd, Cu, and Zn in the acidic soil. Significant reductions in the exchangeable Cd, Cu, Pb, and Zn in both soils were also observed when PG was added. CMP treatments reduced the exchangeable fraction of the heavy metals in most cases. The exception was exchangeable Zn in the calcareous soil, where no significant reduction was observed (Table 6).

For the calcareous soil, treatments of mineral materials generally reduced exchangeable metals in the sequence of Pb > Cd > Cu > Zn. In this respect, exchangeable Pb and Cd were significantly decreased when soils were amended by CMP, PG, or AL at application rates of 2% and 5%. Exchangeable Cu was significantly decreased when soils were amended by PG at application rates of 2% and 5%, or by CMP or AL at application rates of 5%. Exchangeable Zn was significantly decreased only when soils were amended by 5% of PG or AL. In general, the reduction in exchangeable fraction of heavy metals in the soils amended with different mineral materials followed the sequence of CMP, PG > AL > RP. When mineral materials were applied at rate of 2%, the sequence of reduction in exchangeable fractions was CMP (50.53%) > PG (37.63%) > AL (29.03%) > RP (0%) for Cd, PG (32.76%) > AL (18.97%) > CMP (15.52%) > RP (0%) for Cu, CMP (66.67%) > PG (57.14%) > AL (19.05%) > RP (0%) for Pb, and PG (16.13%), AL (16.13%) > CMP (4.83%) > RP (0%) for Zn. When mineral materials were applied at rate of 5%, the sequence of reduction in exchangeable fractions was CMP (70.97%) > PG (62.36%)

Table 3 Chemical fractions of Cd in amended soils (%)

Treatment	Rate (g/kg)	Calcareous soil					Acidic soil				
		EXE	CAB	OXB	OMB	RES	EXE	CAB	OXB	OMB	RES
CO	0	9.3 a	14.6 b	31.4 a	14.8 a	29.9 b	19.6 a	9.9 b	31.6 b	19.5 a	19.4 d
RP1	20	9.3 a	13.9 b	32.1 a	13.2 ab	30.0 b	16.3 ab	10.7 ab	31.4 b	17.8 a	23.8 c
RP2	50	8.9 ab	14.2 b	31.8 a	13.7 ab	28.7 b	13.2 b	11.6 ab	32.7 b	18.4 a	24.1 c
AL1	20	6.6 b	16.7 ab	30.7 a	14.1 a	28.8 b	12.6 b	10.8 ab	35.6 a	18.6 a	22.4 c
AL2	50	5.3 bc	18.3 a	31.2 a	13.6 ab	30.2 b	9.6 c	11.3 ab	38.4 a	18.3 a	22.6 c
PG1	20	5.8 b	13.7 b	29.6 a	14.2 a	36.7 a	8.7 c	10.3 b	32.2 b	19.1 a	29.7 b
PG2	50	3.5 d	14.4 b	30.8 a	13.6 ab	37.7 a	6.8 cd	11.4 ab	31.8 b	19.3 a	30.7 ab
CMP1	20	4.6 c	13.6 b	32.7 a	12.7 b	36.4 a	9.5 c	10.1 b	30.4 b	18.6 a	31.4 a
CMP2	50	2.7 d	13.1 b	31.6 a	13.2 ab	39.4 a	5.3 d	12.2 a	31.7 b	18.1 a	32.7 a

Mean values followed by the same letter within a column are not different at $p < 0.05$ by Fisher's protected least significant difference.

EXE: exchangeable metal; CAB: carbonate associated metal; OXB: oxide associated metal; OMB: organically-bound associated metal; RES: residual metal.

Table 4 Chemical fractions of Cu in amended soils (%)

Treatment	Rate (g/kg)	Calcareous soil					Acidic soil				
		EXE	CAB	OXB	OMB	RES	EXE	CAB	OXB	OMB	RES
CO	0	5.8 a	4.3 b	31.1 a	28.6 a	30.2 c	16.1 a	5.8 b	27.8 b	24.7 a	25.8 c
RP1	20	5.8 a	4.5 b	30.5 a	27.6 a	31.6 c	13.2 b	6.6 ab	27.4 b	22.8 ab	30.0 bc
RP2	50	5.4 a	4.7 b	31.6 a	28.1 a	30.2 c	11.8 b	6.9 ab	29.2 ab	21.6 b	30.5 bc
AL1	20	4.7 ab	6.3 a	30.1 a	26.7 a	32.2 c	11.7 b	5.4 b	30.8 a	22.3 ab	29.8 bc
AL2	50	4.2 b	7.6 a	29.7 a	26.9 a	31.6 c	9.6 c	5.6 b	33.1 a	21.2 b	30.5 bc
PG1	20	3.9 b	3.7 b	28.4 a	27.7 a	36.3 b	10.4 bc	6.3 ab	26.6 b	20.8 b	35.9 ab
PG2	50	2.7 c	3.6 b	28.1 a	26.1 a	39.5 a	8.2 c	7.2 a	25.8 b	20.1 b	38.7 a
CMP1	20	4.9 ab	5.4 ab	29.6 a	28.3 a	31.8 c	12.3 b	6.6 ab	26.4 b	21.3 b	33.4 b
CMP2	50	4.1 b	6.6 a	28.7 a	26.8 a	33.8 bc	10.4 bc	7.9 a	26.1 b	20.9 b	34.7 b

Mean values followed by the same letter within a column are not different at $p < 0.05$ by Fisher's protected least significant difference.

Table 5 Chemical fractions of Pb in amended soils (%)

Treatment	Rate (g/kg)	Calcareous soil					Acidic soil				
		EXE	CAB	OXB	OMB	RES	EXE	CAB	OXB	OMB	RES
CO	0	2.1 a	5.0 b	38.3 a	23.2 a	31.4 b	7.9 a	2.8 b	43.4 a	22.4 a	23.5 c
RP1	20	2.1 a	5.3 b	39.4 a	22.5 a	30.7 b	5.3 b	2.7 b	43.2 a	21.7 a	27.1 b
RP2	50	2.0 a	5.2 b	37.6 a	21.6 a	33.6 ab	4.6 b	2.9 ab	42.8 a	22.3 a	27.4 b
AL1	20	1.7 ab	6.2 ab	37.8 a	22.3 a	32.0 ab	6.4 ab	3.8 ab	41.4 a	22.6 a	25.8 bc
AL2	50	1.4 b	8.4 a	36.4 a	20.4 a	33.4 ab	5.8 ab	4.3 a	42.2 a	21.0 a	26.7 b
PG1	20	0.9 b	5.9 b	37.1 a	21.4 a	34.7 a	4.6 b	2.9 b	42.7 a	19.7 a	30.1 ab
PG2	50	0.5 c	6.6 ab	38.2 a	19.7 a	35.0 a	3.2 bc	3.4 ab	41.6 a	18.6 a	33.2 a
CMP1	20	0.7 bc	6.8 ab	37.4 a	22.6 a	32.5 ab	3.9 bc	3.1 ab	41.8 a	20.4 a	30.8 ab
CMP2	50	0.4 c	7.4 ab	37.1 a	20.8 a	34.3 a	2.8 c	3.5 ab	40.6 a	18.7 a	34.4 a

Mean values followed by the same letter within a column are not different at $p < 0.05$ by Fisher's protected least significant difference.

Table 6 Chemical fractions of Zn in amended soils (%)

Treatment	Rate (g/kg)	Calcareous soil					Acidic soil				
		EXE	CAB	OXB	OMB	RES	EXE	CAB	OXB	OMB	RES
CO	0	6.2 a	7.7 b	35.5 a	15.2 a	35.5 c	14.6 a	1.3 c	42.3 a	12.8 a	29.0 c
RP1	20	6.2 a	8.6 b	33.4 a	17.5 a	34.2 c	12.3 ab	2.2 bc	39.9 a	13.1 a	32.4 bc
RP2	50	6.2 a	8.9 b	32.7 a	16.9 a	35.2 c	10.4 b	4.4 b	38.8 ab	11.9 ab	34.5 b
AL1	20	5.2 ab	11.1 a	31.4 a	14.6 ab	37.7 bc	8.8 c	5.9 b	39.9 a	13.3 a	32.2 bc
AL2	50	4.6 b	13.1 a	30.8 a	12.6 ab	38.9 b	6.6 c	7.9 a	40.9 a	11.2 ab	33.5 b
PG1	20	5.3 ab	6.6 b	32.6 a	13.1 ab	42.4 a	9.5 bc	2.1 bc	38.9 ab	12.1 a	37.3 a
PG2	50	4.9 b	6.1 b	31.4 a	13.3 ab	44.2 a	7.7 c	2.5 bc	37.7 b	12.5 a	39.6 a
CMP1	20	5.9 ab	12.0 a	32.5 a	11.0 b	38.7 b	11.3 b	3.9 b	39.7 a	10.6 ab	34.6 b
CMP2	50	5.5 ab	12.7 a	31.6 a	10.4 b	39.7 b	10.2 b	5.5 b	38.8 ab	8.8 b	36.8 ab

Mean values followed by the same letter within a column are not different at $p < 0.05$ by Fisher's protected least significant difference.

> AL (43.01%) > RP (4.30%) for Cd, PG (53.45%) > CMP (29.31%) > AL (27.59%) > RP (6.89%) for Cu, CMP (80.95%) > PG (76.19%) > AL (33.33%) > RP (4.67%) for Pb, and AL (25.81%) > PG (20.97%) > CMP (16.13%) > RP (0%) for Zn.

For the acidic soil, treatments of mineral materials reduced exchangeable metals in the order of Cd > Pb > Cu > Zn. Exception of few cases, exchangeable Cd, Cu, Pb and Zn were significantly decreased when soils were amended by any of four mineral materials at application rates of 2% and 5%. In general, the reduction in exchangeable fraction of heavy metals for application of different mineral materials decreased in the sequence of CMP, PG, AL > RP. When mineral materials were applied at rate of 2%, the sequence of reduction in exchangeable fractions was PG (55.61%) > CMP (51.53%) > AL (35.71%) > RP (16.83%) for Cd, PG (35.40%) > AL (27.30%) > CMP (23.60%) > RP (18.01%) for Cu, CMP (50.63%) > PG (41.77%) > RP (32.91%) > AL (18.99%) for Pb, and AL (39.73%) > PG (34.93%) > CMP (22.60%) > RP (15.75%) for Zn. When mineral materials were applied at rate of 5%, the sequence of reduction in exchangeable fractions was CMP (72.96%) > PG (65.31%) > AL (51.02%) > RP (32.65%) for Cd, PG (49.07%) > AL (40.40%) > CMP (35.40%) > RP (26.71%) for Cu, CMP (64.56%) > PG (59.49%) > RP (41.77%) > AL (26.58%) for Pb, and AL (54.79%) > PG (47.26%) > CMP (30.14%) > RP (28.77%) for Zn.

Application of mineral materials also had effects, in different extent, on carbonate-bound, oxide-bound, organic matter bound, and residual fractions of heavy metals in the soils (Tables 3, 4, 5, and 6). RP treatments significantly increased residual fraction of Cd, Pb, and Zn, carbonate-bound fraction of Zn, and decreased organic matter bound

fraction of Cu in the acidic soil. However, RP addition did not affect carbonate-bound, oxide-bound, organic matter bound, and residual fractions of heavy metals in the calcareous soil. AL treatments showed higher carbonate-bound fraction of Cd, Cu, Pb, and Zn, and residual fraction of Cd, Pb, and Zn, especially at high rate (5%). It also increased oxide-bound fraction of Cd and Cu in the soils. PG addition to soil increased residual fraction of Cd, Cu, Pb, and Zn, and consequently decreased the organic matter fraction of Cu in the soils. Significant increases of residual Cd, Cu, Pb, and Zn in the soils were also observed after addition of CMP to soils. A exception was residual Cu in the calcareous soil, which did not show significant effect due to CMP addition (Table 4). In addition, application of CMP also increased carbonate-bound fraction of Cu and Zn in the soils.

2.3 Effect of amendment application on leachability of heavy metals in the soils

The concentrations of heavy metals in leachates from columns decreased as the leaching water volume increasing (Fig. 1). The higher released rate of Cd, Cu, Pb, and Zn was generally found in the first several leachings. Addition of mineral materials had significant effects of the metal concentrations in the leachates from the first four leachings.

For the calcareous soil, the concentrations of Cd, Cu, Pb, and Zn in the leachates decreased generally in the sequence of CO, RP > AL > PG, CMP. The concentration of Cd in the first four leachates from the soils amended with AL, PG, and CMP was significant lower than that of the CO. However, there was no significant difference in the concentration of Cd in the leachates between RP

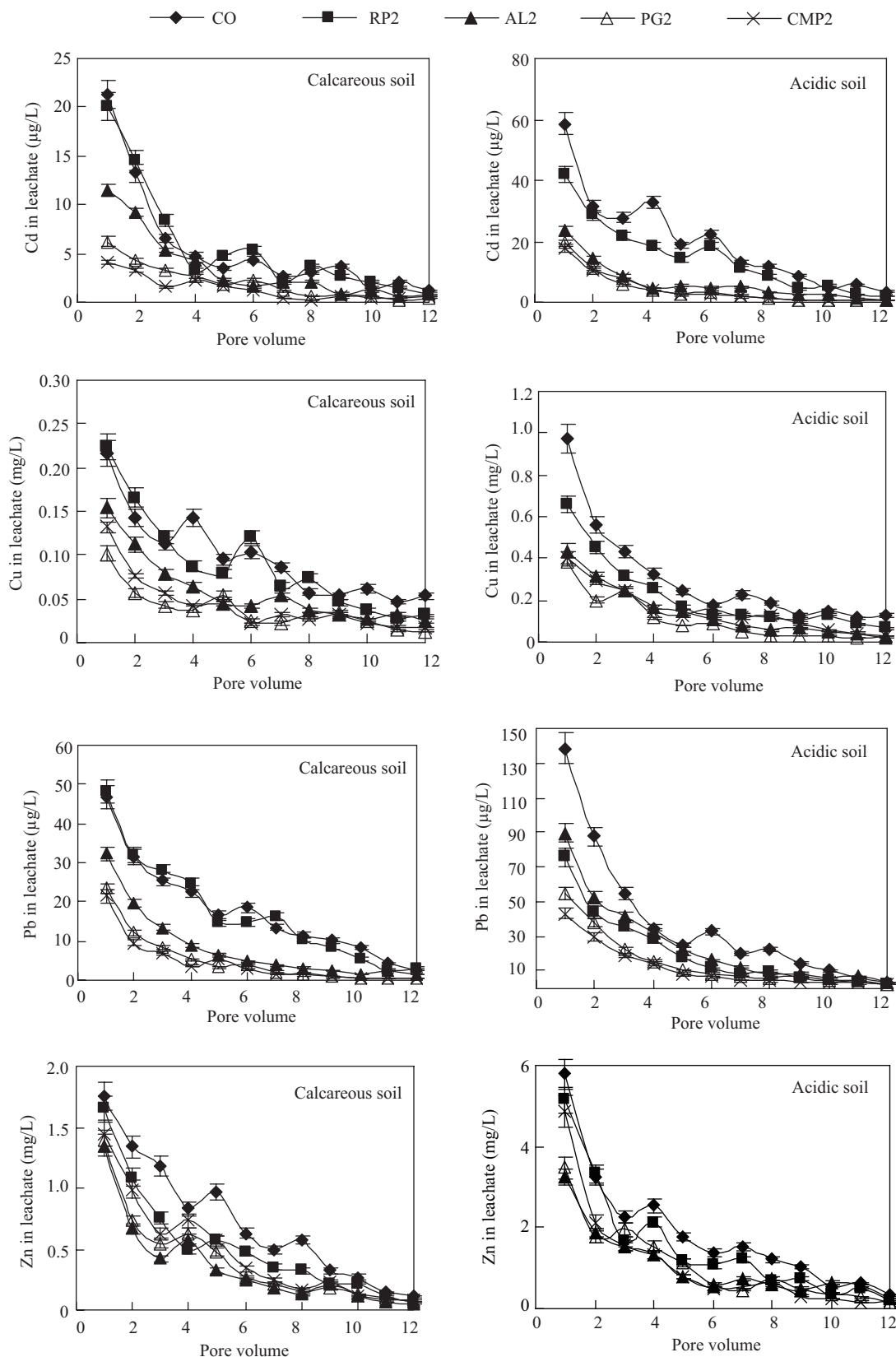


Fig. 1 Concentrations of Cd, Cu, Pb, and Zn in leachates from soil columns amended with different amendment as a function of pore volume. Error bars present standard error.

and CO. The concentrations of Cu and Pb in the leachates from the soils amended with AL, PG, and CMP were significant lower than that of the CO. There was no significant difference in the concentration of Cu and Pb in the leachates between RP and CO. The concentration of Zn

in the most of leachates from the soils amended with RP, AL, PG, and CMP were significant lower than that of the CO, with a fewer exception.

For the acidic soil, application of RP, AL, PG, and CMP could, in general, decrease the concentration of heavy

Table 7 Total amounts of dissolved metals leached from the soils in 12 leachings (unit: mg/column)

Treatment	Calcareous soil				Acidic soil			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
CO	0.054 a	0.94 a	0.17 a	2.92 a	0.191 a	6.89 a	0.36 a	17.82 a
RP2	0.053 a	0.86 a	0.17 a	2.09 a	0.142 b	5.06 b	0.20 b	14.53 b
AL2	0.033 b	0.56 b	0.08 b	1.38 b	0.061 c	3.47 d	0.24 b	10.02 c
PG2	0.019 c	0.37 c	0.05 c	1.04 c	0.042 d	3.90 cd	0.14 c	10.34 c
CMP2	0.013 c	0.42 bc	0.04 c	1.47 b	0.040 d	4.50 c	0.11 c	10.57 c

Mean values followed by the same letter within a column are not different at $p < 0.05$ by Fisher's protected least significant difference.

metals in the leachates. The reduction extent of heavy metals in the leachates decreased generally in sequence of PG, and $CMP > AL > RP$. The results suggested that all of amendments could decrease leaching of the heavy metals in the soil.

Cumulative amounts of dissolved Cd, Cu, Pb, and Zn leached from the soils in 12 leaching varied greatly (Table 7). For the calcareous soil, cumulative amounts of heavy metals leached from the soils decreased in the order of $CO, RP > AL > PG > CMP$ for Cd, Cu, and Pb, and $CO, RP > CMP > AL > PG$ for Zn.

As compared with control, application of RP, AL, PG, and CMP reduced metals leaching by 1.98%, 38.89%, 64.81% and 75.93% for Cd, 8.51%, 40.42%, 60.64% and 55.32% for Cu, 1.76%, 52.94%, 70.00% and 74.12% for Pb, and 28.42%, 52.74%, 64.38% and 49.66% for Zn.

As compared with control, application of CMP, PG, AL, and RP reduced metals leaching by 26.56%, 49.64%, 43.40% and 34.68% for Cu, 44.44%, 33.32%, 61.11% and 69.44% for Pb, and 18.46%, 43.77%, 41.98% and 40.68% for Zn.

3 Discussion

Contaminant immobilizing amendments decrease heavy metal element solubility and leaching by inducing various sorption processes: adsorption to mineral surfaces, formation of stable complexes with organic ligands, surface precipitation and ion exchange. Precipitation as salts and co-precipitation can also contribute to reducing contaminant mobility. The solubility and mobility of heavy metals in soils is quite different and therefore the risk of leaching into groundwater. Different sorption/dissolution processes are influenced by many factors: pH, redox potential, type of soil constituents, cation exchange capacity, etc. and a single mechanism rarely accounts for the immobilization of heavy metals in soil. The fixation efficiency depends on not only the amount of the amendments mixed to the soil, but also the species of the metals. Cation mobility is one of the most important properties that can evaluate their environmental fate. Different metals have the distinct mobilities and certainly it is not easy to find the uniform fixation agents to reduce the bioavailability of heavy metals. Lead is considered the least mobile heavy metal in non-acid soils, even under reduced condition. Complexation with organic matter, chemical sorption on oxides and silicate clays and precipitation as carbonate, hydroxide or phosphate are the mechanisms responsible for lead immobilization. All those immobilizations were

favoured at high soil pH. The behaviour of copper is similar to that of lead, being also sorbed strongly on oxides, silicate clays and humus, and increasingly so as the pH is raised. Above pH 6 its precipitation as hydroxide, oxide or hydroxy-carbonates is also possible (McBride, 1994). Nevertheless, under high pH conditions soluble hydroxy, carbonate and organic matter complexes are formed, and thus increase significantly its mobility. Under acidic conditions, zinc, unlike lead and copper, is one of the most soluble and mobile of the trace metal cations, being held in exchangeable forms on clays and organic matter. At high pH, however, chemical sorption on oxides and aluminosilicates and complexation with humus lowers its solubility markedly. Cadmium is even more soluble than zinc in acidic conditions. This high mobility is attributed to the fact that cadmium sorbs rather weakly on organic matter, silicate clays and oxides unless the pH is higher than 6 (McBride, 1994). A common method for immobilisation of metals in soil is to apply lime, phosphates or organic matter residues (Bolan and Duraisamy, 2003). Soil pH is one of the most important factors that can affect the mobility and bioavailability of heavy metals in soil (Evans et al., 1995). Although liming is primarily aimed at ameliorating soil acidity, it is increasingly being accepted as a management option for reducing the mobility or solubility of potentially toxic metals in soil (Bolan and Duraisamy, 2003). Brallier et al. (1996) observed reduction in soluble and exchangeable Cd and Zn upon liming. Considering the solubility data known for several sparingly soluble Cu, Pb, Cd, or Zn compounds of likely formation in the soil systems (Lindsay, 1979), such pH values suggest that precipitation is playing a significant role in the reduction of exchangeable fractions of the metals in the soils. Therefore, addition of carbonate materials such as agricultural limestone, rock phosphate and calcium magnesium phosphate decreased solubility and mobility of the Pb, Cu, Cd, and Zn in the polluted urban soils.

Phosphate-based materials were widely used to stabilize heavy metals in soils to decrease the metal concentration in soil solution, to decrease metal mobility and leachability, and to transform soluble metals to residual (Zhang and Ryan, 1999). However, metal immobilization by the phosphate-based materials is highly dependent on the crystallization system, the origin of the material and its solubility. Some special characteristics of rock phosphate could be responsible for the failure of this material for metal immobilization in the calcareous soil. Brown et al. (2005) also found different responses for several phosphate

amendments in reducing metal availability. The least effective form was rock phosphate. Brown et al. (2005) suggested that the reason was related to the low solubility of rock phosphate as compared to other phosphate forms. Therefore, differences in immobilization of soil heavy metals between rock phosphate and calcium magnesium phosphate in this study could be related with the higher solubility of P in calcium magnesium phosphate. Ruby et al. (1994) indicated that adequate levels of soil phosphate were responsible for the formation of insoluble complexes and the reduction in potentially bioavailable Pb. Experiments involving treatment of metal contaminated soils with rock phosphates (apatite and hydroxyapatite) have shown that formation of metal-phosphate precipitates and minerals reduced heavy metal solubility. Insoluble and geochemically stable lead pyromorphites such as hydroxypyromorphite ($Pb_5(PO_4)_3OH$) and chloropyromorphite ($Pb_5(PO_4)_3Cl$) have been found to control Pb solubility in apatite amended contaminated soils (Ma and Rao, 1997; Zhang and Ryan, 1999). Other researchers have shown that highly soluble phosphate sources (i.e., phosphate salts) enhance the potential for formation of lead pyromorphite compared to rock phosphate (Pierzynski and Schwab, 1993). Ma and Rao (1997) suggested that P sources with higher solubility could be mixed with rock phosphate to increase the effectiveness of lead immobilization in contaminated soils. The addition of soluble phosphates from industrial sources, such as Na_2HPO_4 (Cotter-Howells and Capron, 1996) and pyrophosphate (Xie and MacKenzie, 1990), are also highly effective for forming precipitates and/or increasing sorption of Pb and Zn. Of the soluble P sources, commercial phosphate fertilizers and sodium phosphates are the most readily available material in large quantities required for remediation of contaminated sites. Therefore, application of CMP was more effective to decrease availability of heavy metals than RP. However, in acidic soil, more free phosphorus could be released from RP to act with heavy metals in the soils. Thereby, the immobilization potential of RP was greater in the acidic soil than that in the calcareous soil.

The solubilities of Cu, Pb, Cd and Zn were determined by sequential extraction in the heavy metal-polluted soils and in differently amended soil samples. This method, despite accepted limitations, provided useful evidence for the different heavy metal fixation capability of the amendments considered, notably agricultural limestone, rock phosphate, palygorskite, and calcium magnesium phosphate. In the amended soils the exchangeable fraction of the heavy metals analyzed decreased, while the strongly bounded fractions (carbonate-bound, and oxide-bound, and residual fractions) were increased. Moreover, the addition of all the amendments induced an increase of the “residual” metal form. The results from this study clearly revealed that the pH increase, caused by addition of each of all four amendments, had a major role in increasing the concentration of the strongly bounded fraction of metals. These amendments were the most efficient in reducing heavy metal solubility, particularly for Pb and Cd. The pH increase induced by agricultural limestone, rock

phosphate, palygorskite, and calcium magnesium phosphate firstly favored heavy metal precipitation. Secondly, this could result in an increase in heavy metal sorption by clay minerals such as palygorskite, finally resulting in a reduced concentration of soluble metal. Palygorskite is a hydrated magnesium aluminium silicate mineral with a structure consisting of parallel ribbons of 2:1 layers, and most likely played a key role in increasing the metal adsorbing capacity of the treated soil.

Our results showed that immobilization effects of heavy metals in the soils varied with the types of amendments. CMP and PG treatments were superior to AL and RP for reducing heavy metal elution. This may indicate that different amendments had different mechanisms for reducing metal availability. The reduction found for AL was probably more related with the increase in pH, while that for PG addition was caused by strong metal sorption and increase of soil pH. And the reduction found for RP and CMP was probably more related with both the increase in pH and presence of P. High application rates of soil amendments to soils could provide higher pH value, concentration of free P, and adsorption sites, therefore, amendments at the high rate addition is the most effective for reducing metal availability than low application rate.

4 Conclusions

In summary, we conclude that application of some mineral materials to moderately metal-polluted soils had various degrees of effect in decreasing the availability of Cd, Cu, Pb and Zn, as measured by chemical fractionation of heavy metals and leaching experiment. Palygorskite and calcium magnesium phosphate were generally quite efficient in reducing availability of metal as compared to control, while rock phosphate was only efficient in acidic soils. The effects of rock phosphate in reducing metal availability in the calcareous soil were the least efficient.

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